

A FEASIBILITY ANALYSIS OF STUDIES ON LINEN FROM THE SHROUD OF TURIN USING NUCLEAR MAGNETIC RESONANCE

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ABSTRACT

The possibility of developing future investigations on the Turin Shroud by means of nuclear magnetic resonance (NMR) is discussed in the present article.

Various traditional techniques such as the static spectroscopy in homogeneous or non-homogeneous magnetic fields or the “Magic Angle Spinning (MAS)” technique and more innovative techniques such as “Cross-Polarisation”, that allows a better signal-to-noise ratio in ^{13}C atoms, are here considered and discussed.

These techniques are applied to recent linen samples to show the possibility of detecting the ^1H and ^{13}C atoms concentration in the Turin Shroud.

Other investigation techniques, to be developed in future, are discussed; among them, the evaluation of other atoms such as ^{14}N or a comparative analysis between NMR results and that obtained from the radioactivity mapping in the Shroud by means of a Geiger-Müller detector.

1) INTRODUCTION

Regarding the Shroud of Turin (ST) some questions exist which scientists until now could not answer in a scientifically acceptable way. Probably the two most important are the dating of the cloth and the explanation as to how the image of the body was formed.

The results of the radiocarbon dating^[1], which declared the Shroud to be an object of medieval origin are doubtful. The effect of the Cambéry fire^[2] and the presence of a bioplastic coating^[3] could in fact form elements able to cause a systematic error in the dating of up to a thousand years.

Diverse hypotheses already have been made about the mechanisms of the formation of the body image, among them energetic effects connected with the resurrection^[4], the effect of aloe and myrrh which interacted with the perspiration of the body wrapped in the cloth^[5], chemical effects by the contact between the body and the cloth analogous to that noticed in the herbaria^[6], the scorching^[7], etc. Behalf the first hypothesis which is difficult to test because of its partly religious character, these hypotheses are demonstrated to be unacceptable. Particular characteristics of the body image could not be reproduced in respective experiments.

To search a solution for these and other problems the development of an analysis is required which goes hand in hand with the development of certain techniques of analysis. A technique which might deliver additional information is one based on research by means of Nuclear Magnetic Resonance, applied either to the whole cloth or to samples of limited dimensions taken from the ST e.g. to carry out a radiocarbon dating.

Nuclear Magnetic Resonance (NMR) allows the measurement of the concentration of atoms in a sample, if these atoms are characterised by a nuclear spin different from zero. For instance the isotopes ^1H , ^{13}C , ^{14}N and ^{15}N possess this property and are present on the linen of the ST.

NMR is based on an alignment of the spins of the investigated atoms parallel to a strong and constant external magnetic field, overlapped by a second impulsive field orthogonal to the first one and oscillating with frequencies able to excite the atomic nuclei.

This non-invasive method is applicable to the linen of the ST without the possibility of damaging it. The magnetic interaction per spin reaches even at the strongest possible magnetic field of 14 T (Tesla, [T] is the SI unite of the magnetic induction) only energy of the order of maximally 10^{-24} - 10^{-25} J, which is negligibly to the thermal interaction energy per spin at ambient temperatures, which is of the order of 10^{-20} - 10^{-21} J .

2) POSSIBLE TYPES OF NMR ANALYSES

Based on the experience in the fields of medicine and biology^[8] it seems to be possible to use the method of Nuclear Magnetic Resonance to execute some scientific experiments on the ST. The aim of the present work is to verify experimentally with the help of samples of recent linen, whether certain types of analysis are possible, which are:

-1) the NMR tomography on the entire cloth, analogous to medical tomography on the human body, which allows one to measure the variation of the concentration of atoms as a function of their position. Technically a construction of spectrometers working with a field of maximally 4T^[8] is possible.

-2) NMR measurements in samples of dimensions of the order of centimetres. For measurements of this type there already exist instruments able to generate magnetic fields up to 14 T. The larger the magnetic field, the better is the resolution of the received signal. The signal intensity shows in fact a quadratic dependence of the magnetic field. The signal-to-noise ratio is proportional to the square root of the acquisition time, to enhance the signal-to-noise ratio by e.g. a factor of 10 it is necessary to enhance the acquisition time by a factor of 100.

Two types of instruments exist:

-a) instruments working with an inhomogeneous field, with the purpose of receiving information relative to the spatial distribution of certain atoms,

-b) instruments which allow one to record signals in magnetic fields of high homogeneity with the purpose of visualising the chemical composition of the sample.

Because of the interaction between the analysed nuclei and their chemical surrounding, one observes a shift of the resonance frequency. This so called chemical shift is characteristic of the respective position of the atom in the chemical structure. Usually the chemical shift is measured as part per million (ppm), defined by:

$$[ppm] = \frac{w_s - w}{w_s} 10^6 \quad (1)$$

with w the measured resonance frequency of a certain peak and w_s the resonance frequency of a reference substance. Theoretically the chemical shift of ^1H atoms can vary between -1 ppm and 12 ppm and the chemical shift of ^{13}C atoms between -10 ppm and 240 ppm^[9].

The proposed analyses could be used for studying the following aspects on ST:

-a) study of the spatial distribution of the ^{13}C concentration, using NMR tomography, to carry

out before a possible repetition of the radiocarbon dating. This could help to select a suitable position for cutting a piece out of the ST for the analysis,

-b) preventive study using NMR, with higher accuracy, of the concentration of ^{13}C , ^{14}N , etc., executed on eventual samples which are provided for the radiocarbon dating to receive a dating with higher quality;

-c) execution of an NMR tomography to establish the spatial distribution of ^1H , ^2H , ^{14}N and ^{15}N inside the cloth; a comparison between the concentration of a certain type of atoms in correspondence to the body image relative to the medium concentration in the cloth would allow one to test the hypotheses which assume the existence of an energy source (e.g. neutrons) as the reason for the image formation^[4];

-d) dating of the linen of the ST (independently of the radiocarbon analysis) using the results received at point (b) also for other types of atoms. This is based on the fact that the cellulose of the linen undergoes reactions with the environment. Under the influence of light and thermal sources it aggregates chromophoric groups^[11] which cause the yellowing of the linen. Eventually one observes significant differences comparing the concentrations of atoms present in recent and ancient linen. Until now, possible resolutions and accuracies of this method are not evidenced.

-e) experimental simulation of the effects of fire on the ^{13}C concentration in linen samples

3) EXPERIMENTAL DEVICES

The experiments have been carried out with NMR spectrometers of the type Bruker-MSL500 and Bruker-MSL300 at the Faculty of Physics and Earth Sciences of the University of Leipzig.

The NMR spectrometers use a cryomagnet to generate a magnetic field of respective 11,7 T and 7 T inside the coil .

The magnetic induction inside the coil can be considered as constant, a possible variation of 10^{-5} T is negligibly small (the magnetic field is induced by a perpetual current in the superconducting coil).

The resonance frequency of the ^1H atoms amounts to respective 500 MHz and 300 MHz.

From equation (1) follows that a spectral resolution (difference of the position of two spectral lines on the frequency axis) of 1 ppm corresponds to a difference of the resonance frequency of 500 Hz or 125 Hz respective for ^1H and ^{13}C spectroscopy with the spectrometer Bruker-MSL500.

The optimal dimension of samples to insert into the interior of the coil of such spectrometers amounts to about, 0,5-1 cm³, or, in case of linen samples, to about 20 mg.

The quality of intensity measurements obtained with the NMR spectrometer Bruker-MSL500 is as follows:

- uncertainty of repeatability: $\pm 1\%$;
- uncertainty of reproducibility: $\pm 5\%$;
- uncertainty because of non-corrected systematic effects (e.g. ambient humidity): $\pm 10\%$;
- uncertainty of reproducibility of the chemical shift: $\pm 1\text{ppm}$.

4) RESULTS

At the University of Leipzig experimental tests have been carried out on samples of recent linen with the aim of executing a feasibility analysis by evidencing the accuracy of the obtained results in function of the accumulation time.

In fact a limit of NMR analyses is the relative elevated time (which may be hours or days) necessary to obtain sufficient resolutions, especially for atoms with relatively low concentration in

linen.

The results described here refer only to analyses of the ^1H and ^{13}C ; other analyses, e.g. of the isotope ^{14}N , which are also interesting from a scientific point of view, will be eventually considered in future works. Actually the expected signal-to-noise ratio is too low to receive suitable results.

4.1) Static ^1H NMR spectroscopy

Only the ^1H nuclei of linen samples produce a clearly distinguishable signal. A few seconds are sufficient to obtain an suitable result.

We used 4 scans of each 1 s. The optimum duration of one scan is about 5 times the longitudinal relaxation time T_1 , the time necessary for the spin to turn back to its position of the thermal equilibrium after an excitation.

The obtained results show that the linewidth of the peak is about 15 ppm. In consideration of the fact that the chemical shift of ^1H can theoretically only vary between -1 a 12 ppm, ^1H is consequently less applicable for structural explorations of linen.

To receive narrower lines which eventually allows one to distinguish several spectral lines is only possible by applying a rapid sample rotation, the so called Magic Angle Spinning, MAS^[10]. Consequently an NMR tomography on the entire ST can be applied with the aim to measure the spatial distribution of the concentration of ^1H nuclei.

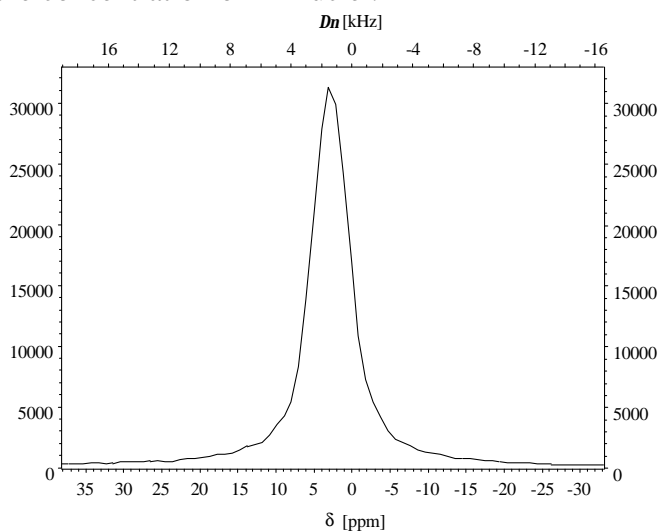


Fig.1: Spectrum of a linen sample of 20 mg analysed by ^1H NMR with the spectrometer MSL500 after 4 scans of each 1 s. The chemical shift d is indicated both in ppm and in the corresponding variation of the resonance frequency Dn in kHz for the spectrometer MSL500. The intensity values are given in arbitrary units. The signal-to-noise ratio amounts to about 500. The graphic shows the Fourier transform of the “Free Induction Decay” acquired in the time domain.

Provided that the concentration of ^1H atoms differs between the body image area and the other parts of the cloth by 10% or more, it would be possible to obtain an “NMR image” which could be compared with the visible image.

In figure 1 one example of the results obtained with a sample of recent linen (delivered by the firm “Johann Jatzwauk - Lausitzer Laden“, Hoyerswerda/Germany) of about 20 mg is reported. The analysis has been carried out by ^1H NMR with the spectrometer MSL500, by application of 4 scans with a length of each 1 s (corresponds to 5 times the relaxation time of the considered

atom, which is about 200 ms).

The values indicated in figure 1 are expressed in arbitrary units (it is not usual to use a certain unit for the intensity of NMR signals); to obtain information regarding the effective percentage of ^1H atoms respective to the total mass of the linen sample, comparing measurements of calibration samples are necessary. Such analyses could be carried out in successive studies.

4.2) Static Spectroscopy of ^1H isotopes: measurements of relaxation times

For ^1H isotopes it is possible to measure the relaxation times (the time necessary for the spin to turn into its position of thermal equilibrium after an excitation).

These kinds of experiments^[10], carried out by measuring the signal intensity in function of the duration of one scan, are also possible in inhomogeneous magnetic fields like those used for the tomography.

The relaxation times depend on the intensity of the outer magnetic field and on the temperature during the measurement (the measurements took place at room temperature after heating the sample).

With the spectrometer MSL500 the following relaxation times were measured:

- in normal linen samples: $0,7 \text{ s} \pm 0,1 \text{ s}$.
- in samples heated at $140 \text{ }^\circ\text{C}$ for 1200 s (this temperature does not cause visible variations of the sample surface): $1,0 \text{ s} \pm 0,1 \text{ s}$;
- in samples heated at $300 \text{ }^\circ\text{C}$ for 100 s (the heat caused a complete change of the sample colour into brown): $1,3 \text{ s} \pm 0,1 \text{ s}$;

4.3) Static Spectroscopy of ^1H isotopes: analyses of systematic effects

It has been stated that the humidity of the linen samples and of the environment is a parameter which can influence the spectroscopy of ^1H isotopes in a non-negligible way. The protons of water present on the cloth form an important part of the spectrum.

To test this hypothesis, which is evidenced by the results discussed in §4.2 too, an analysis on diverse linen samples was carried out. The following samples have been compared:

- sample A: linen not treated at ambient temperature;
- sample B: linen heated at $200 \text{ }^\circ\text{C}$ for 1200 s;
- sample C: linen heated at $200 \text{ }^\circ\text{C}$ for 2400 s;
- sample D: linen heated at $300 \text{ }^\circ\text{C}$ for 60 s.

The samples B and C show a yellowing of the linen fibres, the sample D show after short time a uniform change of the colour into brown. We obtained the following results:

- sample A: signal intensity of 1000 ± 50 units;
- sample B: signal intensity of 150 ± 15 units;
- sample C: signal intensity of 100 ± 15 units;
- sample D: signal intensity of 100 ± 15 units.

This result leads to the assumption that at least 80% of the ^1H NMR signal of a non-treated sample is caused by the presence of water or other volatile components contained in the chemical structure of the linen. For this reason it will be necessary to control not only the temperature but also the ambient humidity before starting an NMR analysis on the ST.

4.4) Static Spectroscopy of ^{13}C isotopes

Because of the possible broad variation of the chemical shift of the spectral lines from -10 to 240

ppm^[9] the analysis of the concentration of atoms ¹³C is very suitable from the chemical point of view to explore the molecular structure. Moreover ¹³C NMR spectroscopy is also very important if one intends to set up a multidisciplinary research of the effective concentration of ¹²C, ¹³C and ¹⁴C with the aim of a dating of linen samples.

Unfavourable aspects of ¹³C are the low natural concentration of this isotope of only 1,1% of all carbon atoms, and the low gyromagnetic ratio of only $6,7 \cdot 10^7 \text{ T}^{-1} \text{ s}^{-1}$, (¹H has a gyromagnetic ratio of $2,7 \cdot 10^7 \text{ T}^{-1} \text{ s}^{-1}$, the signal intensity is proportional to the third power of the gyromagnetic ratio). Static experimental tests have demonstrated the difficulties in applying the method. To obtain a signal-to-noise ratio of 2 about 10 hours of signal acquisition are necessary. To improve the signal-to-noise ratio by a factor two to the amount of S/R=4, an acquisition time of 40 hours are necessary, because of the quadratic relation between signal-to-noise ratio and acquisition time.

4.5) Cross Polarisation of ¹³C isotopes

One can obtain better results by utilisation of the “Cross Polarisation”^[10] which is based on a simultaneous excitation of ¹H and ¹³C nuclei. In doing this the energy of the ¹H is transferred to the ¹³C spins resulting in an amplification of the ¹³C signal.

The amplification depends on the chemical composition of the sample, especially on the position and the mobility of the atoms in consideration. Therefore the proportion of the intensities of two spectral lines is in general not identical to the concentration of the matching nuclei. The chemical shift however does not change.

The Cross Polarisation also permits a qualitative analysis of changes in the chemical structure of the sample after possible treatments, comparing the intensities of lines of the same chemical shift before and after the treatment.

As a consequence one can obtain a double information executing a comparative study of several parts of the cloth of the ST:

- a) analysis of the ¹³C peak intensity for evaluating the concentration;
- b) analysis of the ¹³C peak position for evaluating possible changes in the chemical structure of the linen

In figure 2 a first result (which certainly could be improved by optimising the procedure) is reported which shows a signal-to-noise ratio of 6. This result is obtained after 40 hours (corresponding to 408000 scans of each 3 s).

The spectrum shows one line or peak with a chemical shift of 80 ± 5 ppm and a linewidth of 100 ± 10 ppm (the great uncertainty of the linewidth depends also on the effect of “leakage” typical for Fourier transformations).

The typical chemical shift for single carbon-oxygen bounds is about 48-85 ppm^[9]. The observed signal matches them. Only triple carbon-carbon bounds produce chemical shifts which lie in the same area, at about 75-95 ppm^[9]. Signals of single carbon-carbon bounds are situated between 5-60 ppm^[9] and signals of double carbon-carbon bounds between 105-145 ppm^[9].

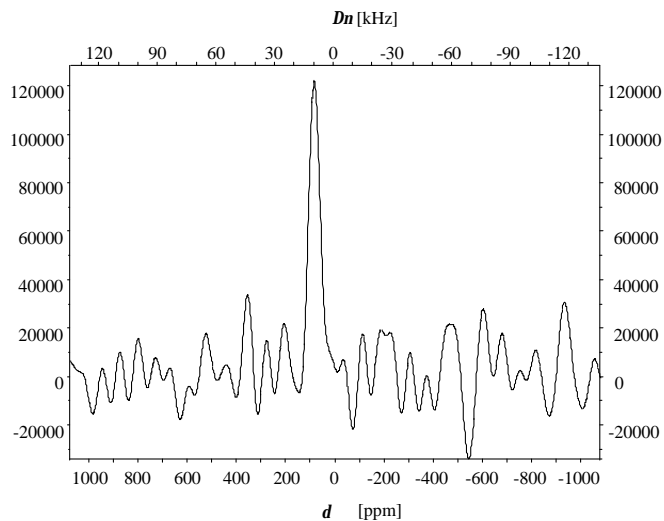


Fig.2: Spectrum of a linen sample of 20 mg analysed by ^{13}C Cross Polarisation NMR in the spectrometer MSL500 after 408000 scans of each 3 s (= 40 hours). The chemical shift d is indicated both in ppm and in the corresponding variation of the resonance frequency Dn in kHz for the spectrometer MSL500. The peak has a position of 83 ppm and a linewidth of ca. 100 ppm. The signal-to-noise ratio amounts to about 6. The graphic shows the Fourier transformation of the “Free induction Decay” acquired in the time domain.

5) OTHER POSSIBLE RESEARCH TECHNIQUES

The present study is a preliminary analysis of some techniques of nuclear magnetic resonance applied on samples of linen to verify the feasibility of future analyses on the ST. However further developments and also other experimental methods are possible which could not be foreseen in this preliminary analysis for financial reasons.

5.1) Other Types of possible NMR studies

With the help of the following innovative technique of NMR analysis diverse scientific points of interest for the ST could be regarded:

- a) experiments with linen samples to determine the concentration of ^1H and ^{13}C atoms using MAS NMR (Magic Angle Spinning) ^[10]. Using this technique it is possible to reduce the linewidth of the peak. This method works with the help of a fast rotation of the linen samples of small dimensions (order of centimetres) inside the spectrometer. The higher economic expense of this method is due to the necessity of special rotors.
- b) simulation of effects of fire on the percentage of ^{13}C in the linen by help of ^{13}C enriched with CO and CO₂ (to increase to a high degree the signal-to-noise ratio) and eventually of catalysts like cations of silver (which were present in the environment of the ST during the fire of Chambéry). It is also possible to do an analysis of eventual mutations of the chemical structure of the linen. ^{13}C enrichment of the immersing material allows one to decide whether these changes are caused by immersion or by material belonging to the original linen structure.
- c) observation of the effect of bioplastic coating^[3] on linen fibres: one could biologically induce the generation of bioplastic coating using samples of new linen immersed in an ^{13}C enriched ambient. The advantages are identical to those of point b).
- d) observation of the effect of radiation on the concentration of ^1H and ^{13}C atoms: alpha, beta

and gamma radiation are not expected to have a strong effect on the concentration of atoms, neutronic radiation however could induce relevant variations. Actually the use of neutronic sources is not available. In the future it could be interesting to carry out such analyses for testing the hypothesis of an impression of the body image by a neutronic source ^[4].

-e) analysis of the effect of possible neutronic radiation^[4] or of alpha radiation on the chemical composition of linen: to execute such studies it is proposed to divide a cloth of recent linen into 6 equal pieces of each about 1 m²; the first 2 pieces are the control samples, two pieces will be exposed to neutronic radiation and the other two to alpha radiation of diverse intensity. After this an analysis by ¹H, ¹³C, ¹⁴N NMR will be carried out to observe eventual radiation effects on the chemical environment of these nuclei, for example one could determine the proportion between single and double carbon bounds. The observations have to be compared with results received from thermally treated samples.

5.2) Mapping of the radioactivity of the ST:

To consolidate studies regarding point (d), a parallel measurement of the radioactivity with the help of a Geiger-Müller counter, which is available at the University of Leipzig too, should be carried out. Such counters allow repetition rates of measurements of the order of kHz.

To test the feasibility of this parallel analysis, it is suggested to treat samples of recent linen in suitable accelerators (e.g. at the Hahn-Meitner-Institut Berlin/Germany) by rays of diverse quantities of neutronic radiation and to do successive analyses of the remaining radioactivity by particle counters and of the concentration of atoms by NMR.

After verifying the feasibility, portable Geiger-Müller counters could be used to carry out a two-dimensional mapping of the radioactivity on the ST. Using computers it will be possible to reconstruct a two-dimensional map of the radioactivity present on the cloth with the resolution of the order of square decimetres.

If one obtains a uniform radioactivity on the ST, which is similar to those of normal linen samples, the hypothesis of radiation as the reason for the forming of the picture could eventually be disproved, on the other hand, if one finds a higher radioactivity in the image area and a lower on other parts of the cloth, the result could be regarded as a proof for the radiation hypothesis.

6) COMMENTS

The study of feasibility has shown the following aspects:

-a) It is possible to carry out an analysis of nuclear magnetic resonance on ¹H atoms: the corresponding signal is characterised by a signal-to-noise ratio of more than 20, but the humidity of the environment and the cloth forms a parameter which can induce systematic effects of up to 80%. That is why it would be necessary to store the ST in a controlled environment already some hours before starting a possible acquisition. At the moment an analysis of the concentration of ¹H atoms does not seem to be a very useful tool for the scientific studies on the ST, in contradiction of an analysis of the concentration of ¹³C or ¹⁴N atoms that is more important. On the other hand the execution of such ¹H measurements is relatively easy and could eventually illuminate new scientific aspects which have not been considered until now. The signal belonging to ¹H atoms is essentially stronger than signals of other atoms present on the ST.

An analysis of the concentration of ¹H atoms could also be used to plot the content of water on the linen.

-b) It is possible to carry out an analysis of nuclear magnetic resonance on ¹³C atoms: even if the corresponding signal is characterised by a low signal-to-noise ratio of about 6. Using innovative

techniques like the Cross Polarisation, a further optimisation and improvement is eventually possible.

The analysis of the concentration of ^{13}C atoms can be useful in the future in a possible multidisciplinary study based on the ^{14}C radiocarbon dating.

-c) It could be important to visualise the distribution of the concentration of ^{14}N atoms on the ST, because the result could eventually help to confirm the hypothesis of an image formation by an “energy lamp”^[4].

The possibility of measuring the concentration of atoms characterised by a weak signal like ^{14}N is in the phase of investigation. A helpful method could be a Cross Polarisation using the ^1H atoms to amplify the ^{14}N signal. A ^{13}C - ^{14}N Cross Polarisation, however, will be more difficult because the amount of the necessary bounds between ^{13}C and ^{14}N is rare.

-d) The preliminary results show the necessity of having samples of the ST for longer times at one's disposal (even some days).

On one hand researchers continue to study the possibility of utilising techniques which allow to obtain the same results in shorter times by searching for methods to reduce the noise.

On the other hand researchers attempt to find possibilities to execute fast experiments on the whole ST, or to execute longer experiments on samples of small dimensions, eventually at samples intended for a successive radiocarbon dating.

CONCLUSIONS

A feasibility analysis has been developed regarding the possibility of executing future research on linen of the ST using nuclear magnetic resonance.

Diverse techniques have been taken into consideration like static spectroscopy, “Magic Angle Spinning - MAS”, using a fast rotation of the sample, and the innovative technique of “Cross Polarisation” which allows to obtain a better signal-to-noise ratio.

Besides the NMR relaxation time of ^1H atoms has been measured.

These techniques have been applied to samples of recent linen of dimensions of the order of square centimetres. The obtained results in terms of concentration of ^1H and ^{13}C atoms have been discussed as a function of ambient effects which could influence the results.

Particularly the measurements of ^1H atoms, executed using traditional techniques, have shown a signal-to-noise ratio higher than 20, while the measurements of ^{13}C atoms carried out using “Cross Polarisation” have shown a signal-to-noise ratio of about 6. The last result can be optimised.

The measured chemical shift of the analysed atoms is compatible with the values known from the literature.

The relative uncertainty of the measurements is 10% if one controls some systematic effects: the diverse concentration of water absorbed by the fibres of the linen and the ambient humidity can vary the results relative to the concentration of ^1H by about 80%.

Some other research techniques have been presented and discussed which could be developed in the future; among them the measurement of the concentration of other atoms like ^{14}N or a comparative analysis of the results obtained by nuclear magnetic resonance and by a radioactivity mapping of the whole ST.

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